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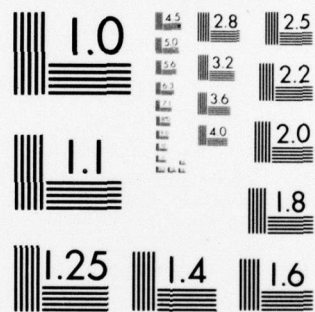
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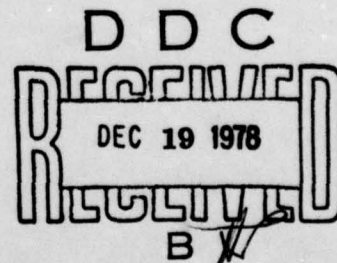
Aging Behavior of Crude Shale Oil

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Crude shale oil produced by the Paraho retort was heated for eight weeks at 50°C. This corresponds to at least one year of storage at ambient conditions. Increases in oil viscosity and in the content of high molecular weight compounds were observed, but pour point changes were minimal. The overall changes at the experimental conditions used are modest.		

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AGING BEHAVIOR OF CRUDE SHALE OIL

INTRODUCTION

Crude shale oil exhibits instability and degradation with age (1). This behavior is not unexpected since shale oil, formed by a thermal process, contains high concentrations of olefins (2,3). In addition, shale oil contains large amounts of nitrogen, sulfur, and oxygen compounds (2,3). Olefins can undergo polymerization reactions and the nitrogen, sulfur, and oxygen compounds readily oxidize. Free radical processes are involved in both types of reactions. The oxidation processes include coupling and thus compounds with higher molecular weights can form via the oxidation reactions as well as by olefin polymerization.

The extent to which these polymerization and coupling reactions occur affects the selection of refining processes for conversion of crude shale oil to refined products. For instance, the U. S. Navy is accumulating shale oil at the rate of 150-200 barrels per day (bpd) from the 8 1/2 foot diameter Paraho retort (4). Approximately a year and one-half will be needed to produce the goal of 100,000 barrels. Therefore, a substantial portion of the crude will be in storage for over one year prior to the conversion into military fuels. If significant polymerization and/or dimerization occurs during this storage period, the refining efforts will have to include greater reliance on cracking processes to produce middle distillate fuels.

FUEL STORAGE CONDITIONS

In order to shorten the time required to monitor chemical changes in storage, the fuels were stressed at 50°C. This temperature affords about an 8-fold increase in reaction rates compared to 20°C which is taken as a realistic average year around ambient temperature. This modest acceleration should not significantly alter the relative rates of the various reactions occurring in fuel aging.

Two crude shale oils were stressed in these experiments. Both samples were produced in the 8 1/2 foot diameter above ground Paraho retort (4), one produced in the direct fire mode and the second in the indirect mode. Each crude was exposed in one quart brown bottles with an initial ullage of 50 percent.

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Two bottles of each oil were aged, one in the presence of air and the second with nitrogen in the vapor space. The bottles were cooled to room temperature at the end of each two week period, flushed with air or nitrogen as desired, capped with a screw top closure, and returned to the 50°C oven. The bottles were sampled after one week. Since little change was observed after this period, the unaerated bottles were not sampled again until the conclusion of the stress at 8 weeks. The aerated oils were sampled at 1, 2, 4, and 8 weeks.

ANALYTICAL TECHNIQUES

The shale oil samples were monitored for viscosity changes. This measurement was done in a capillary viscometer at 50°C, a temperature about 20°C above the initial pour points of the two oils.

The pour point was performed according to ASTM method D97-66(5).

Instrumental techniques applied to the shale oils were infrared spectroscopy, gas chromatography, reversed phase liquid chromatography, and gel permeation chromatography (GPC). Only the latter technique, which separates components by molecular weight, indicated any distinct differences between the stressed and unstressed materials.

The GPC analyses were performed with tetrahydrofuran solvent, μ -Styragel columns, and an ultraviolet detector set for a wavelength of 294 millimicrons. Two column combinations were utilized. The most useful joined two 25 cm long 100 Å columns in series. The second arrangement had one 1000 Å, one 500 Å, and two 100 Å columns in series.

The columns were calibrated for molecular weight vs retention time with polystyrene (MW-2350) and a series of polyphenylethers (MW's-170, 262, 446, 630).

RESULTS AND DISCUSSION

The viscosity for all four samples increased during the eight week heating period at 50°C. The data in Table I indicate that the increase continued throughout the period. Thus the aging reactions were still occurring after eight weeks.

The viscosity increase was greater for the two aerated samples but a definite viscosity change was also observed for the samples heated in the absence of air. The shale crude oil produced by the direct Paraho process had a higher initial viscosity than the indirect process crude oil. The direct process oil exhibited a somewhat greater viscosity increase with aging than did the indirect process oil. This finding applied to both the aerated and air-free exposures.

The pour points of the four samples exhibited little or no change over the eight week heating period. The direct process shale oil stayed the same but the indirect oil increased slightly in pour point.

The GPC analyses indicated some increase in high molecular weight (MW) material in the heated samples. These analyses examined primarily the direct process oil which had been aerated since this sample showed the greatest change in viscosity. Both GPC column combinations demonstrated the MW increase but the 4-column combination had only an enlarged shoulder on the leading edge of the GPC trace. The 2-column combination (2-100Å) gave a distinct peak for the high MW material. This peak corresponds to the compounds that are too large to enter the pores of the gel packing. These excluded materials come out as a sharp peak as indicated in Figure 1. Using the polyphenylethers as a MW guide, the exclusion limit is found to be 800-900.

Figure 1 has two chromatograms which are shifted slightly with respect to each other. The narrow trace represents direct process shale oil prior to heating and the heavy trace represents this oil after 8 weeks of heating in the presence of air. The broad peak decreased with heating while the sharp peak increased. Measurement of the peak areas showed that the sharp peak was $5.3 \pm 0.4\%$ of the total for the unheated oil and $8.0 \pm 0.4\%$ for the heated oil.

The GPC results support the viscosity data indicating some larger compounds are formed in the aging process. The GPC data is semi-quantitative at best, however, since (a) the absorption coefficients of the oil components are not known and (b) a significant portion of the compounds in shale oil (saturated and substituted benzene hydrocarbons) do not absorb at 294 millimicrons. Nonetheless, we can conclude that the increase in material with MW above about 850 is quite modest.

The fact that a definite but different viscosity increase was observed for the aerated and air-free samples shows that both polymerization and oxidation reactions are taking place during the heating period. Although both types of reactions are occurring, a judgment on the relative importance of the two cannot be made on the basis of the available data.

The changes measured in this study show that shale oil does undergo definite chemical reactions during aging. These reactions reveal themselves by changing properties which indicate that higher molecular weight products are formed. The changes and the amount of higher MW material formed are modest, however, for periods of 8 weeks at 50°C. Changes in storage at ambient conditions for one year should not exceed those at 50°C for 8 weeks. We conclude that one year ambient storage should require no alteration of refining processes.

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TABLE I
Viscosity of Stressed Shale Crude Oil

Heating Period (Weeks) *	Viscosity (centistokes at 50°C) **			
	Direct Process Oil		Indirect Process Oil	
	No Air	Aerated	No Air	Aerated
0	20.7	20.7	15.5	15.5
1	21.5	22.1	15.6	16.4
2	--	23.0	--	16.6
4	--	24.4	--	17.4
8	26.2	27.0	16.9	18.8
% change in 8 weeks	+26	+30	+ 9	+22

* At 50.0±0.2°C

** Viscosity Measurement Reproducibility - ±0.04cS

TABLE II

Pour Point of Stressed Shale Crude Oil

Heating Period (Weeks) *	Pour Point (°C) **			
	Direct Process Oil		Indirect Process Oil	
	<u>No Air</u>	<u>Aerated</u>	<u>No Air</u>	<u>Aerated</u>
0	29	29	27	27
1	29	29	27	27
8	29	29	28	29

* At $50.0 \pm 0.2^\circ\text{C}$ ** Pour Point Reproducibility - $\pm 1^\circ\text{C}$

FIGURE I

GEL PERMEATION CHROMATOGRAM

SHALE OIL

